

PART ONE
DIMESITYLCARBINOL

PART TWO
ADDITION OF BENZYL MAGNESIUM CHLORIDE TO
2-METHOXYQUINOLINES

BY
HAROLD LEONARD JACKSON

B.A., University of Wichita, 1943
M.S., University of Wichita, 1946

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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PART ONE

DIMESITYLCARBINOL

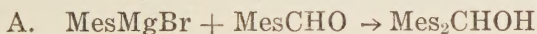
INTRODUCTION

The presence of a dimesitylmethyl group may confer upon a compound properties unlike those of analogs containing aryl groups other than mesityl (1,2). Since dimesitylcarbinol, in contrast to dimesityl ketone, readily takes part in metathetical reactions (3), it can be considered a parent substance for the preparation of compounds containing the dimesitylmethyl group. According to Lapkin (4) the attempted synthesis of dimesitylcarbinol from mesitylmagnesium bromide and ethyl formate gives dimesityl ketone and dimesitylmethane rather than the expected carbinol.

It was the purpose of this investigation to study this anomalous reaction of mesitylmagnesium bromide and ethyl formate as well as the unusual behavior of compounds containing the dimesitylmethyl group. Attention was directed also to the peculiar hindrance effects provided by two mesityl groups attached to a single carbon atom.

DISCUSSION OF RESULTS

Dimesitylcarbinol was prepared in good yield from mesitylmagnesium bromide by the following two new methods:



The formation of dimesitylcarbinol by method B was not accompanied by the anomalous products reported by Lapkin (4). This reaction between a hindered Grignard reagent and ethyl formate proved to be a good method of preparation for both didurylcarbinol and di-(4-methoxy-2,6-xylyl)-carbinol.

Dimesitylcarbinol as well as the corresponding chloride is converted readily to a carbonium ion possessing a high degree

of stability. This was demonstrated by dissolving the carbinol in 100 per cent sulfuric acid to give a deep red solution which yielded a quantitative amount of the methyl ether of dimesitylcarbinol when poured into cold methanol. The ease of carbonium ion formation must be attributed to the high degree of electron release of the two mesityl groups.

Although dimesitylchloromethane does not form a Grignard reagent, it can serve as an alkylating agent. Diethyl dimesitylmethylmalonate was formed by treating magnesiomalonic ester with dimesitylchloromethane. The structure of this ester was established by hydrolysis and decarboxylation to β,β -dimesitylpropionic acid. This acid was prepared also by the hydrolysis of ethyl β,β -dimesitylpropionate. The preparation of this latter ester was made possible by the suprising discovery that mesitylmagnesium bromide could be added easily in a 1,4-manner to ethyl 2,4,6-trimethylcinnamate.

Attempted alkylation of aniline hydrochloride or phenol with either dimesitylcarbinol or dimesitylchloromethane led to high-melting hydrocarbons having the composition of tetramesitylethylene. This compound, however, showed none of the typical reactions of an ethylene, resisted ozonization and could not be hydrogenated. When it was oxidized with sodium dichromate in concentrated sulfuric acid, acetic acid was the only product identified. Treatment of didurylcarbinol with aniline hydrochloride and acetic acid gave an analogous hydrocarbon while less hindered carbinols formed no such products.

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PART TWO

ADDITION OF BENZYL MAGNESIUM CHLORIDE TO 2-METHOXYQUINOLINES

INTRODUCTION

The replacement of the methoxyl portion of an ester group by the action of a Grignard reagent is a well-established reaction. It has been demonstrated further that a methoxyl group activated by a carbonyl or cyano group on an aromatic carbocyclic compound can be replaced by the radical of a Grignard reagent (1,2). In this study it was proposed to extend this replacement reaction to the quinoline series in view of the close analogy between the alkoxylactim structure found in 2-methoxyquinolines and the structure of an ester group.

DISCUSSION OF RESULTS

When an excess of benzylmagnesium chloride in ether solution was treated with an ether solution of 2-methoxyquinoline, the product isolated by distillation after hydrolysis of the reaction mixture was a colorless, viscous oil. This oil was hydrolyzed readily by a very dilute solution of hydrochloric acid. A microquantitative analysis of the products indicated that the methoxyl group was not replaced as had been anticipated. The benzylmagnesium chloride had added in a 1,4-manner to the 2-methoxyquinoline to give 4-benzyl-1,4-dihydro-2-methoxyquinoline, which is tautomeric with the more stable 4-benzyl-3,4-dihydro-2-methoxyquinoline. The presence of the readily hydrolyzed iminoester grouping in this latter compound explains the easy and rapid hydrolysis of the benzyl adduct to 4-benzylhydrocarbostyryl.

This same series of reactions were carried out with benzylmagnesium chloride and 2-methoxylepidine, and analogous products were obtained. The addition of the benzyl group to the 4-position of 2-methoxylepidine was striking since this addition took place on a nuclear carbon atom already substi-

tuted with an alkyl group. No reaction was noted between an ethereal solution of phenylmagnesium bromide and 2-methoxylepidine.

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VITA

The author was born in Wichita, Kansas, on March 13, 1923, and attended the public schools of that city. In September, 1940, he entered the University of Wichita and was graduated in chemistry from that school in August, 1943. After two semesters of graduate study at the University of Wichita, he was inducted into the Army in June, 1944. Upon his discharge from the Army in February, 1946, he returned to the University of Wichita and completed his work for the Master of Science degree in July, 1946. In September, 1946, he entered the Graduate College of the University of Illinois where he held a University Fellowship from September, 1946, to June, 1947, and a part-time teaching assistantship during the summer of 1947. From September, 1947, until June, 1948, he held the Rohm and Haas Company Fellowship and from September, 1948, to June, 1949, the Socony-Vacuum Oil Company Fellowship.



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